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(54) Titre : PELLICULE PROTEINIQUE ADHESIVE POUR EMBALLAGE
(54) Title: PROTEIN ADHESION FILM FOR PACKAGING

(57) Abrégé/Abstract:

In general, the instant invention relates to protein adhesion cook-in films (1) having a protein adhesion sealing layer of polymer having carboxylic acid moieties and (2) wherein said sealing layer does not require metal ionomer cross-linking in order to exhibit protein adhesion. More particularly, it relates to a thermoplastic film comprising a thermosealing layer selected from ethylene-methacrylic acid copolymers (EMAA) having a methacrylic acid content of about 4 to about 18% by weight, and ethylene-acrylic acid copolymers (EAA) having an acrylic acid content of about 4 to about 22% by weight. The sealing layer has improved sealing and strength properties, as well as protein adhesion characteristics.

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ABSTRACT OF THE INVENTION

In general, the instant invention relates to protein adhesion cook-in films (1) having a protein adhesion sealing layer of polymer having carboxylic acid moieties and (2) wherein said sealing layer does not require metal ionomer cross-linking in order to exhibit protein adhesion. More particularly, it relates to a thermoplastic film comprising a thermosealing layer selected from ethylene-methacrylic acid copolymers (EMAA) having a methacrylic acid content of about 4 to about 18% by weight, and ethylene-acrylic acid copolymers (EAA) having an acrylic acid content of about 4 to about 22% by weight. The sealing layer has improved sealing and strength properties, as well as protein adhesion characteristics.

PROTEIN ADHESION FILM FOR PACKAGING

Field of the Invention

In general, the instant invention relates to protein adhesion cook-in films (1) having a sealing layer of polymer having carboxylic acid moieties and (2) wherein the sealing layer does not require metal ionomer cross-linking of the polymer having carboxylic acid moieties in order to exhibit protein adhesion. More particularly, it relates to a film comprising a thermosealing layer selected from ethylene-methacrylic acid copolymers (EMAA) having a methacrylic acid content of about 4 to about 18% by weight, and ethylene-acrylic acid copolymers (EAA) having an acrylic acid content of about 4 to about 22% by weight. Surprisingly it has been found that after cook-in of a food product, the film has protein adhesion characteristics. The protein adhesion characteristic of the thermosealing layer of the instant films cause them to stick, i.e. bindingly adhere, to a food product cooked in a package of the film.

Background of the Invention

This invention relates to the field of flexible plastic films for packaging, and more specifically to such films which are thermosealing, whether heat-shrinkable or not, as well as to container structures made from such films and to packages, particularly for food items, using such films and containers. The

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use of plastic films for packaging items in general, and foods in particular, is widespread nowadays. Depending on the performance to be achieved, the films typically comprise various plastic layers which, according to their chemical composition and the consequent properties, do perform the required function.

As thermosealing layers various polymeric materials have been used heretofore, among which the most widely used have been, for example, ethylene-vinyl acetate (EVA) copolymers, various ethylene polymers such as very low density linear polyethylene (VLDPE), or ionomeric copolymers such as those available under the trademark Surlyn (R) from E.I. duPont de Nemours Inc., Co. (USA). These latter ionomeric polymers generally consist of copolymers of ethylene and methacrylic acid or copolymers of ethylene and acrylic acid which copolymers are ionically cross-linked so as to convert them into metal salts, just designated as ionomers.

Notwithstanding the fact that such polymers used heretofore as thermosealing layers gave sufficiently satisfactory performance, they still had disadvantages which limited their use in certain applications. In particular, none of these polymers showed a sufficiently broad spectrum of properties comprising both a good sealability in the presence of contamination and of creases or folds in the sealing area as well as a good seal strength together with a wide sealing range in terms of temperature or time, and also protein adhesion characteristics.

Blends of 80 to 90% ethylene/acrylic acid copolymer (EAA) with the remainder being linear low density polyethylene (LLDPE) are shown in U.S. Patent 4,678,836 (Dow Chemical).

From U.S. Patent 3,365,520 (duPont), U.S. Patent 4,399,181, (Asahi-Dow), or U.S. Patent 4,414,053 (Gulf) films are known that comprise blends of ethylene-methacrylic acid (EMAA) with Surlyn, with ethylene methyl acrylate (EMA) or with other polymers, for use in forming oriented multilayer

tion, which are suitable both for cold packaging and for cook-in with protein adhesion of the packaged food items.

These and other objects which will appear more clearly from the following disclosure are achieved by a flexible, thermoplastic film for cook-in packaging according to this invention having a thermosealing layer comprising a copolymer of (i) an alpha-olefin having the formula $RCH=CH_2$ wherein R is H or C_1 to C_{20} alkyl, C_1 to C_{20} alkoxy, or C_6 aryl, and (ii) an alpha,beta-ethylenically unsaturated carboxylic acid. Preferably, the thermosealing layer comprises a copolymer selected from ethylene-methacrylic acid (EMAA) copolymers, ethylene-acrylic acid (EAA) copolymers, or mixtures thereof. More preferably, the thermosealing layer comprises a copolymer selected from ethylene-methacrylic acid (EMAA) copolymers with a methacrylic acid (MAA) content of about 4 to about 18% by weight, ethylene-acrylic acid (EAA) copolymers with an acrylic acid (AA) content of about 4 to about 22% by weight, or mixtures thereof.

This invention is based on the discovery that a polymer containing carboxylic acid moieties, such as an EMAA or EAA copolymer as defined above, gives rise to a film for use as thermosealing layer, particularly in multilayer films, which has an excellent combination of properties, surprisingly including protein adhesion from cook-in of a food product. The sealing layer does not require the presence of the related metal salt cross-linked ionomeric materials, many of which are sold as Surlyn by du Pont, in order to give rise to the protein adhesion characteristic.

Most preferably, the thermosealing layer according to this invention comprises said EMAA copolymer with a MAA content of about 4 to about 15% by weight, e.g. of about 12% by weight, or said EAA copolymer with an AA content of about 6 to about 12% by weight, or a blend of such copolymers in any proportion.

According to further embodiments of the invention the thermosealing layer comprises a blend of about 10 to about 99% by weight of the polymer containing carboxylic acid moieties, such as the EMAA or EAA copolymer as defined above, with about 90 to about 1% by weight of a polyolefinic polymer or copolymer. Preferably, the thermosealing layer comprises a blend of about 30 to about 70% by weight of the polymer containing carboxylic acid moieties, such as the EMAA or EAA copolymer as defined above, with about 70 to about 30% by weight of a polyolefinic polymer or copolymer. Polyolefin includes but is not limited to, linear low density polyethylene, linear very low density polyethylene, ethylene alkyl acrylate copolymers (such as ethylene-butyl acrylate, ethylene-ethyl acrylate, or ethylene-methyl acrylate), ethylene-vinyl acetate, ethylene-vinyl acetate modified with functional groups, and mixtures thereof.

These polymers are abbreviated herein as follows:

ethylene-methacrylic acid	EMAA
ethylene-acrylic acid	EAA
linear low density polyethylene	LLDPE
linear very low density polyethylene	VLDPE
ethylene-butyl acrylate	EBA
ethylene-ethyl acrylate	EEA
ethylene-methyl acrylate	EMA
ethylene-vinyl acetate	EVA

Statement of Invention

Therefore, the present invention provides a flexible thermoplastic film suitable for protein-adhesion cook-in packaging comprising a thermosealing layer of a copolymer of (i) an alpha-olefin having the formula $RCH=CH_2$ wherein R is H or C_1 to C_{20} alkyl, C_1 to C_{20} alkoxy, or C_6 aryl, and (ii) an alpha,beta-ethylenically unsaturated carboxylic acid.

The present invention also provides a cook-in structure for packaging made of the film described in the above paragraph, which is sealed together at two portions of said thermosealing layer arranged adjacent and facing each other. The present invention also provides a method for making a protein adhesion cook-in package comprising enveloping a food product in the film described in the above paragraph, removing air from inside the thus obtained package, sealing the package by thermosealing together at least two portions of the thermosealing layer facing each other, and subjecting the sealed package to cooking at high temperature, whereby the thermosealing layer adheres to the food product. The present invention also provides a cooked, protein-adhesion, cook-in package comprising a food product enveloped in the film described in the above paragraph, the film being sealed together by at least one thermoseal at two portions of said thermosealing layer facing each other, the sealed package having been subjected to cooking at high temperature, whereby the thermosealing layer bindingly adheres to the food product. These cook-in structures or packages are bags, casings, pouches, and the like. As mentioned, there is a thermoseal. The food product is then put inside the bag, casing, pouch, et cetera, and prior to cook-in, the other end may be simply folded over, or may be sealed such as by another thermoseal or by a clip. Then the package of food is cooked.

Detailed Description of the Invention

The thermosealing layer comprises a polymer containing carboxylic acid moieties. By "polymers containing carboxylic acid moieties" as that term is used herein it is intended to mean copolymers of (i) an alpha-olefin having the formula $RCH=CH_2$ wherein R is H or C_1 to C_{20} alkyl, C_1 to C_{20} alkoxy, or C_6 aryl, and (ii) an alpha,beta-ethylenically unsaturated carboxylic acid. Preferably, when R is alkyl, it is C_1 to C_8 alkyl. Also, preferably, the alpha,beta-ethylenically unsaturated carboxylic acid is present in an amount by mol % of about 50% or less, more preferably about 30% or less, most pref-

erably about 20% or less. Further, by the term "polymers containing carboxylic acid moieties" it is intended to include carboxylic acid-forming moieties such as anhydrides.

The acid copolymer need not necessarily comprises a two component polymer. Thus, although the olefin content of the acid copolymer preferably is at least 50 mol percent, more than one olefin may be employed. Also, other copolymerizable monoethylenically unsaturated monomers may be employed in combination with the olefin and the carboxylic acid comonomer. It is intended also to include terpolymers. Accordingly, acid copolymers or terpolymers suitable for use in the present invention include, but are not limited to, ethylene/acrylic acid copolymers, ethylene/methacrylic acid copolymers, ethylene/itaconic acid copolymers, ethylene/methyl hydrogen maleate copolymers, ethylene/maleic acid copolymers, styrene/maleic acid copolymers, styrene/maleic half ester copolymers, alkyl vinyl ether/maleic acid copolymers, alkyl vinyl ether/maleic half ester copolymers, ethylene/methyl hydrogen maleate/ethyl acrylate terpolymers, ethylene/methacrylic acid/vinyl acetate terpolymers, ethylene/acrylic acid/vinyl alcohol terpolymers, ethylene/propylene/acrylic acid terpolymers, ethylene/styrene/acrylic acid terpolymers, ethylene/acrylic acid/methyl methacrylate terpolymers, ethylene/methacrylic acid/ethyl acrylate terpolymers, ethylene/itaconic acid/methyl methacrylate terpolymers, ethylene/methacrylic acid/acrylonitrile terpolymers, ethylene/fumaric acid/vinyl methyl ether terpolymers, ethylene/vinyl chloride/acrylic acid terpolymers, ethylene/vinylidene chloride/acrylic acid terpolymers, ethylene/vinyl fluoride/methacrylic acid terpolymers, and ethylene/chlorotrifluoroethylene/methacrylic acid terpolymers.

The copolymer of an alpha-olefin having the formula $RCH=CH_2$ wherein R is H or C_1 to C_{20} alkyl, C_1 to C_{20} alkoxy, or C_6 aryl, and an alpha,beta-ethylenically unsaturated carboxylic acid representatively may be produced by the copolymerization of ethylene and a carboxylic acid comonomer there-

for such as acrylic acid or methacrylic acid. Preferably, when R is alkyl, it is C₁ to C₈. Suitable such acid copolymers are the Primacor (TM) polymers, supplied by Dow Chemical Company, Midland, Michigan. Primacor is produced by the copolymerization of ethylene and acrylic acid (EAA). A very suitable Primacor polymer is Primacor 1410 or Primacor 5981. Other suitable such acid copolymers are sold under the trade name Nucrel by duPont; they are produced by the copolymerization of ethylene and methacrylic acid (EMAA). A very suitable Nucrel polymer is Nucrel 1202.

The instant thermosealing layer does not require the presence of ionomer in order to exhibit protein adhesion characteristics. Thus, the "polymers containing carboxylic acid moieties" are to be distinguished from ionomers, namely from the copolymer of an alpha-olefin having the formula $RHC=CH_2$ wherein R is H or C₁ to C₂₀ alkyl, C₁ to C₂₀ alkoxy, or C₆ aryl, and an alpha,beta-ethylenically unsaturated carboxylic acid which are partially neutralized with a suitable metal cation such as zinc cation or sodium cation. These metal salt neutralized copolymers containing carboxylic acid moieties are called ionomers. Ionomers are commercially available as Surlyn(R) from the E.I. duPont de Nemours Company of Wilmington, Delaware, and are described in detail in U.S. Patents 3,355,319 and 3,845,163. Protein adhesion cook-in films having an ionomer sealing layer (i.e. a Surlyn sealing layer) are described in the above-mentioned U.S. 4,469,742 and U.S. 4,606,922.

Typically, in the manufacture of films, a suitable polymer usually in the form of pellets or the like, is brought into a heated area where the polymer feed is melted and heated to its extrusion temperature and extruded as a tubular hot "blown bubble" through an annular die. Other methods, such as "slot die" extrusion wherein the resultant extrudate is in planar, as opposed to tubular form are also well known. If heat shrinkable film is desired, then after extrusion, the film is typically cooled and then reheated and stretched, i.e. oriented by "tenter framing" or by inflating with a "trapped bubble", to

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impart the heat-shrinkable property to the film. For multi-layer films, such as those made by coextrusion of multiple individual resins or blends, a suitable adhesive polymer layer may be employed to promote interlayer adhesion.

The above general outline for manufacturing of films is not meant to be all inclusive since such processes are well known to those in the art. For example, see U.S. Patent Nos. 4,274,900; 4,229,241; 4,194,039; 4,188,443; 4,048,428; 3,555,604; 3,741,253; 3,821,182; and 3,022,543. The disclosures of these patents are generally representative of such processes and are hereby incorporated by reference.

The thermosealing layer of the invention is preferably used in multilayer films comprising at least a second structural layer conferring upon the film mechanical or abuse resistance. Preferably the film of the invention comprises at least the multi-layer structure as follows:

Sealing/Structural/Structural
or
Sealing/Barrier/Structural

The gas barrier layer can be made of materials conventionally used for such purpose, for example of copolymers of vinylidene chloride with vinyl chloride or with methyl acrylate or with both, ethylene-vinyl alcohol (EVOH) copolymers, for example having an ethylene content of 30 to 47%, polyamides or copolyamides or blends thereof with EVOH.

The structural layer which, beyond conferring abuse resistance, also increases the heat-shrink percentage when heat-shrinkable films are prepared, can be selected from polymers including, but not limited to, very low density polyethylene (VLDPE), high density (HDPE), linear low density (LLDPE), ethylene copolymers with vinyl or acrylic comonomers such as ethylene-vinyl acetate (EVA), ethylene-butyl acrylate (EBA), ethylene-methyl acrylate (EMA), ethylene-ethyl acrylate

(EEA), ethylene-methacrylic acid (EMAA), ethylene-acrylic acid (EAA), ionomers, ethylene-propylene random copolymers (EPC), polyethylene (PE), polypropylene (PP) optionally modified with functional groups, polyamides such as Nylon 6, Nylon 6-66, Nylon 6-12, or Nylon 6-69; polyesters, copolyesters, and mixtures thereof. These may also be blended with the thermosealing layer.

Among the ethylene copolymers a preferred copolymer is EVA having a VA content of from 2 to 20% by weight, preferably of from 5 to 12% by weight.

Among the possible blends of the above polymers for producing the structural layer, blends of LLDPE and EVA or of VLDPE and EVA in a weight ratio of 70:30 to 20:80 can be mentioned.

The preferred multilayer film of the invention can comprise, in addition to the above-mentioned layers, further layers, such as adhesive layers, which improve the adhesion between the various functional layers. A structure of this type may comprise the following layers:

Sealing/Adhesive/Barrier/Adhesive/Structural

As adhesive layers, those commonly known for such use can be employed, e.g. EVA copolymers or EVA copolymers modified with acid functional groups. The EVA copolymers useful as adhesives have a high VA content.

Preferably at least the thermosealing layer of a film according to the invention is electron beam cross-linked by irradiation at about 1 to about 15 MR (megarads). It has been found that such treatment notably increases the overall resistance of the obtainable seal, whether cold or hot.

However, it is not necessary to electron-beam irradiate the films of the invention; suitable films may be obtained

often absent any electron beam irradiation. From cook-in, the thermosealing layer, even though it has not been electron beam irradiated, often adheres to the food product. See Examples 5 and 6 below.

According to a specific embodiment of this invention, a whole multilayer film can be irradiated to achieve cross-linking. In this case, the film can be prepared by simultaneous extrusion of all the layers, for example in tubular form, and their subsequent electron beam irradiation treatment. The irradiation may take place on the collapsed tube, or on a slit open lay-flat structure.

According to an alternative embodiment, a multilayer film of the invention is produced by first extruding a substrate comprising the EMAA or EAA thermosealing layer and possible further layers, in particular structural layers, then cross-linking the substrate by electron beam irradiation, and finally extruding onto the irradiatively cross-linked substrate the further layers of the final film.

According to a still further embodiment of the invention, a multilayer film can be prepared by laminating various self-supporting preformed films according to the desired structure, by using intermediate adhesive layers. The above-mentioned adhesive materials can be used for this purpose. Also, in this embodiment part of the laminate, or alternatively the whole laminate may be subjected to electron beam irradiation treatment.

Since for packaging food products it is advantageous to have heat-shrinkable films, the film of the invention may be made heat-shrinkable by orientation through at least a mono-axial stretching in the longitudinal or transverse direction with respect to the direction of extrusion, but preferably through biaxial stretching, using techniques well-known in the field. For example, in the case when the film is prepared by coextrusion in tubular form, the bi-axial stretching can be

performed by the "air bubble" blowing method, on-line or off-line of the extrusion process. The film of this invention, either irradiated or not, has a thickness that depends on the number of layers, for example, typically from about 15 to about 250 microns, preferably from about 40 to about 150 microns.

As used herein the term "extrusion" or the term "extruding" is intended to include coextrusion, extrusion coating, or combinations thereof, whether by tubular methods, planar methods, or combinations thereof.

An "oriented" or "heat-shrinkable" material is defined herein as a material which, when heated to an appropriate temperature above room temperature (for example 90°C), will have a free shrink of about 5% or greater in at least one linear direction.

Melt index was measured in accordance with ASTM D 1238, Condition E.

The term "cook-in package", as used herein, is intended to refer to packaging material structurally capable of withstanding exposure to cook-in time-temperature conditions while containing a food product. Cook-in time-temperature conditions typically imply a long slow cook, for example by submersion in water at 70-80°C for 4-6 hours. Submersion at 80°C for 12 hours probably represents the limiting case. Under such conditions, a packaging material properly characterized as cook-in will maintain heat seal integrity and will be delamination resistant. Typically, cooked "cook-in" packaged foods go directly to the consumer in that configuration and may be consumed with or without warming.

The term "protein adhesion", as used herein, is intended to refer to packaging material which has a sealing layer, that from cook-in exhibits binding adherence to the food product cooked in the packaging material. Binding adherence is demonstrated by the "Cook-In Protein Adhesion Test" described below.

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TEST METHODS

Seal Strength Test:

The bags were tested at about 73°F (about 23°C) (room temperature).

All bag samples were heat sealed at one end on conventional equipment well known in the art of heat sealing of tubing, and a mouth end of each bag was left open.

Each bag was then clamped in a fixture provided with a hose. The open mouth end of each bag was clamped around the hose. Air was pumped through each hose whereby each bag was inflated to the same initial pressure. Then, each fixture retained each inflated bag in air at 23°C, and two sides of each bag were respectively restrained by two metal plates spaced about 10 cm apart. For each bag, the pressure was increased via the hose at the rate of 1 inch of water pressure (2491 dynes/cm²) per second till the heat seal for that bag either leaked or burst open at the IOWP (inches of water pressure) designated below.

Cook-In Protein Adhesion Test (Binding Adherence to Food):

Bags of the film samples were tested for binding adherence to a cooked-in meat product. Each bag was stuffed with turkey emulsion, vacuumized, heat-sealed, and cooked at 55°C for 30 minutes, and then at 60°C for 30 minutes, and then at 65°C for 30 minutes, for a total of 90 minutes cooking time, followed by cooling in an ice bath.

The protein adhesion characteristic of the thermosealing layer of the instant films cause them to stick, i.e. bindingly adhere, to the cooked food product, in this instance turkey.

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A quantitative comparison of the adherence level of several of the samples in relation to that of control samples (samples wherein the food contact layer contained Surlyn) was determined as follows. After cook-in and cooling, each sample was placed in the jaws of a Scott tester CRE 1000, and the force to pull the bag from the meat was measured at a constant crosshead speed. (Another machine commonly used for such measuring is the Instron model 1122 tester.)

Puncture "Impact" Test:

This was performed in accordance with a variation of ASTM-D 3763-84. The impact test was a measure of cold seal strength. A weighted mandrel was allowed to fall into an open bag, impacting the heat seal. The amount of weight needed to break the seal times the height from which the weight was dropped constituted the amount of energy needed to break the seal. The percentage of seals that broke at a specified energy in inch-pounds was recorded.

12 Hour Delamination Test:

Bags were filled with an oil-water emulsion and then heat sealed closed. Then they were heated for 12 hours. Some were heated at 150°F (65.6 °C), some at 160°F (71.1 °C), and some at 170°F (76.7 °C). Some of these were in a high humidity environment at the designated temperature, and some of these were in water at the designated temperature. The % failures of the films was indicated by delamination of the films.

Materials employed in the Examples:

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GENERIC NAME

FOLLOWED

BY TRADE

NAME OF

POLYMER

DESCRIPTIVE INFORMATION

ABOUT THE POLYMER

SUPPLIER

COMPANY

ADHESIVE

Bynel 3062

du Pont

EVOH

EVAL LC-E105A

EVALCA

EPC

DENSITY

KS400

0.90 g/cc

Solvay

Zinc Methacrylate

Ionomer

Type of copolymer

Surlyn 1650

Partially zinc neutralized
ethylene methacrylic acid copolymer

du Pont

EVA

MI

COMONOMER

% VA

LD318.92

2.0

Vinyl Acetate

9

Exxon

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NA-295-00 2.6 Vinyl Acetate 6 USI

<u>EBA</u>	<u>MI</u>	<u>COMONOMER</u>	<u>%BA</u>	<u>DENSITY</u>	
EA719.009	0.35	Butyl acrylate	18.5%	0.926	Quantum/USI

<u>LLDPE</u>	<u>MI</u>	<u>COMONOMER</u>	<u>DENSITY</u>	
Dowlex 2045.03	1.1	Octene	0.920 g/cc	Dow Chemical

<u>EMAA</u>	<u>MI</u>	<u>% By Weight Methacrylic Acid</u>	<u>% By Weight Ethylene</u>	
EMAA-1 Nucrel 1202	2	12	88	du Pont
EMAA-2 Nucrel 0903	3	9	91	du Pont
EMAA-3 Nucrel 0403	3	4	96	du Pont

<u>EAA</u>	<u>MI</u>	<u>% By Weight Acrylic Acid</u>	<u>% By Weight Ethylene</u>	
PRIMACOR 1410	1.5	9.5	90.5	Dow

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PPMIMP

NPP8000gk

5

161°C

Quantum/USI

The following examples show, only for illustrative and not limiting purposes, various structures of films according to this invention.

Example 1 (manufacture of films)

The following biaxially stretch oriented 12:1 films were prepared as described above. Percentages designated were by weight. Samples vary in megarads of irradiation. Thickness of the multi-layer films was about 2.3 to 2.4 mils. In sample numbers 1A, 1B, and 1C, the sealing layer thickness was about 0.54 mils, and in sample number 1D, 1E, and 1F, the sealing layer thickness was about 0.36 mils. In sample number 9A, the sealing layer thickness was about 0.45 mils; in 9B and 9C, it was about 0.35 mils; and in 9D and 9E, it was about 0.55 mils. The composition of each layer is recited below from the sealing layer (on the left) to the abuse layer (on the right). (Samples 3-8 AND 11 were a comparison films.)

Table I

<u>SAMPLE NUMBER</u> <u>(MR IRRADIATION)</u>	<u>COMPOSITION OF EACH LAYER</u>	
1A (3MR)	EMAA-1 /70% LLDPE /30% EVA (9% VA)	/30% LLDPE /70% EVA (9% VA)
1B (5MR)	SAME	
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1C (7MR)

SAME

1D (3MR)

EMAA-1 /70% LLDPE /30% LLDPE
/30% EVA (9% VA) /70% EVA (9% VA)

1E
(5MR)

SAME

1F
(7MR)

SAME

2
(5MR)

EMAA-1 / 70% LLDPE / EPC
/ 30% EVA (9% VA) /

3
(1MR)
COMPARISON

80% LLDPE /30% LLDPE /50% LLDPE
20% Surlyn 1650/70% EVA (9% VA)/50% EVA(6% VA)

4
(1MR)
COMPARISON

85% LLDPE /30% LLDPE /50% LLDPE
15% Surlyn 1650/70% EVA (9% VA)/50% EVA(6% VA)

5
(1MR)
COMPARISON

90% LLDPE /30% LLDPE /50% LLDPE
10% Surlyn 1650/70% EVA (9% VA)/50% EVA(6% VA)

6
(1MR)
COMPARISON

83% LLDPE /30% LLDPE /50% LLDPE
17% Surlyn 1650/70% EVA (9% VA)/50% EVA(6% VA)

7
(4MR)
COMPARISON

Surlyn 1650 /30% LLDPE /50% LLDPE
/70% EVA (9% VA) /50% EVA(6% VA)

8A
(2MR)

EMAA-1 /30% LLDPE /50% LLDPE
/70% EVA (9%VA)/50% EVA (6%VA)

8B
(4MR)

SAME

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9A EMAA-1 / 80%EVA(6%VA) / ADH / EVOH / ADH / 80%EVA(6%VA)
 (3MR) / 20%LLDPE / / / 20%LLDPE
 BDX 2875

9B EMAA-1 / 80%EVA(6%VA) / ADH / EVOH / ADH / 80%EVA(6%VA)
 (3MR) / 20%LLDPE / / / 20%LLDPE

9C EMAA-1 / 80%EVA(6%VA) / ADH / EVOH / ADH / 80%EVA(6%VA)
 (5MR) / 20%LLDPE / / / 20%LLDPE

9D EMAA-1 / 80%EVA(6%VA) / ADH / EVOH / ADH / 80%EVA(6%VA)
 (3MR) / 20%LLDPE / / / 20%LLDPE

9E EMAA-1 / 80%EVA(6%VA) / ADH / EVOH / ADH / 80%EVA(6%VA)
 (5MR) / 20%LLDPE / / / 20%LLDPE

10 Surlyn/ 80%EVA(6%VA) / ADH / EVOH / ADH / 80%EVA(6%VA)
 (4MR) 1650 / 20%LLDPE / / / 20%LLDPE
 COMPARISON

Example 2 (performance evaluation of films of Example 1)

In order to evaluate the performance of a multilayer film according to this invention comparative tests were run relating to the puncture impact, seal strength, delamination, and protein adhesion of the inventive films recited in Example 1 (which had an EMAA thermosealing layer) with respect to that of the comparative multilayer films recited in Example 1 (which did not have an EMAA thermosealing layer). The results are given in the following tables:

Table II(a)

SAMPLE NUMBER	PUNCTURE IMPACT RESULTS ¹	SEAL STRENGTH
	(% FAILURES)	(23°C) (IOWP)
1A	44.0	183.8
1B	13.0	183.8

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1C	2.7	206.8
1D	8.0	158.8
1E	10.7	131.3
1F	0.0	183.5
2	29.0	216.4
3	41.0	136.1
COMPARISON		

¹ Maximum weight and potential energy used of 305.25 inch pounds.

Table II(b)
12 HOUR DELAMINATION
Cook-In Test Results (% Failures)

SAMPLE NUMBER	HIGH HUMIDITY			WATER COOK		
	150°F 12 HRS	160°F 12 HRS	170°F 12 HRS	150°F 12 HRS	160°F 12 HRS	170°F 12 HRS
1A	0.0	0.0	0.0	0.0	30.0	75.0
1B	0.0	0.0	50.0	0.0	27.3	50.0
1C	0.0	0.0	60.0	0.0	0.0	0.0
1D	0.0	12.5	0.0	0.0	0.0	0.0
1E	0.0	0.0	20.0	0.0	0.0	33.3
1F	0.0	0.0	50.0	0.0	0.0	66.7
2	0.0	22.2 (delam)	57.1 (delam)	0.0	100.0 (delam)	100.0 (delam)
3 COMPARISON	0.0	0.0	100.0	0.0	10.0	0.0

NOTE: delam is an abbreviation for delamination.

Table II(c)
Protein Adhesion

<u>SAMPLE NUMBER</u>	<u>NUMBER OF TESTS</u>	<u>ADHESION (g/in) MEAN</u>
3 COMPARISON	6	141.5
4 COMPARISON	8	92.5
5 COMPARISON	8	80.6
6 COMPARISON	8	128.0
7 COMPARISON	8	147.7
8A	6	154.1
8B	5	178.2

From the above results it can be seen that the film according to the invention had a seal strength and a protein adhesion which was notably improved, over that of the control films that had a Surlyn (R) thermosealing layer.

The multilayer film of the invention showed superior properties also with respect to other conventional materials used heretofore as thermosealing layers.

Example 3 (manufacture of films)

The following additional biaxially stretch oriented 12:1 films were prepared as described in Example 1. Percentages designated were by weight. Samples vary in the sealing layer. The composition of each layer is recited below from the sealing layer (on the left) to the abuse layer (on the right).

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Table III

<u>SAMPLE NUMBER</u> <u>(MR IRRADIATION)</u>	<u>COMPOSITION OF EACH LAYER</u>		
10 (4MR) COMPARISON	Surlyn/80%EVA(6%VA)/ 1650 /20%LLDPE	ADH/EVOH/ADH / / / /	80%EVA(6%VA) / 20%LLDPE
11 (4MR)	50% EMAA-1 / 50% LLDPE	70% LLDPE /30% EVA (9% VA)	/30% LLDPE /70% EVA (9% VA)
12 (4MR)	50% EMAA-1 / 50% EVA (6%VA)	70% LLDPE / 30% EVA (9%VA)	/30% LLDPE /70% EVA (9%VA)
13 (4MR)	50% EMAA-1 / 50% EVA (9%VA)	70% LLDPE / 30% EVA (9%VA)	/30% LLDPE /70% EVA (9%VA)
14 (4MR)	EMAA-2 /70% LLDPE /30% EVA (9% VA)	/30% LLDPE /70% EVA (9% VA)	
15 (4MR)	EMAA-3 /70% LLDPE /30% EVA (9% VA)	/30% LLDPE /70% EVA (9% VA)	

Example 4 (performance evaluation of films of Example 3)

In order to evaluate the performance of a multilayer film according to this invention comparative tests were run relating to the protein adhesion of the inventive films recited in Example 3 (which had an EMAA thermosealing layer) with respect to that of the comparative multilayer film recited in Example 3 (which did not have an EMAA thermosealing layer). This test differed from the protein adhesion test method described above in that instead of using turkey emulsion, chunks of turkey which had been cleaned up by removing the extraneous fat and other connective tissue such as partial removal of the sinews were used. (The chunks were cubes about 3 inches on a

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side, which is about 7.6 cm on a side.) The results are given in the following table:

Table IV
Protein Adhesion

<u>SAMPLE NUMBER</u>	<u>ADHESION INDEX*</u>	
	<u>MEAN</u>	<u>STANDARD DEVIATION</u>
10 (4MR) COMPARISON	100.0	± 4.5
11 (4MR)	98.8	± 8.1
12 (4MR)	84.0	± 21.1
13 (4MR)	88.2	± 19.6
14 (4MR)	95.5	± 11.2
15 (4MR)	60.4	± 26.7

$$* \text{Adhesion index} = \frac{\text{adhesion force of sample on Day } n}{\text{adhesion force of Comparison 10 on Day } n} \times 100$$

where the Comparison sample 10 was ambient.

It is noted that sample number 15 worked, but not as well as the others. This sample had a sealing layer of EMAA-3, which, as can be seen from the description above of materials used in the Examples, is an EMAA with only 4% MAA.

Example 5 (manufacture of films)

The following additional unoriented films were prepared by the tubular hot blown method as described above. Percentages designated were by weight. The films were monolayer and thus the entire film was the "thermosealing" layer. None of the monolayer films was electron beam irradiated. The composition of each is recited below.

Table V

<u>SAMPLE</u>	<u>COMPOSITION</u>
1	10% EMAA-1 + 90% LLDPE
2	20% EMAA-1 + 80% LLDPE
3	30% EMAA-1 + 70% LLDPE
4	10% EMAA-1 + 90% EVA (9%VA)
5	20% EMAA-1 + 80% EVA (9%VA)
6	30% EMAA-1 + 70% EVA (9%VA)
7	10% EMAA-1 + 90% EBA
8	20% EMAA-1 + 80% EBA
9	30% EMAA-1 + 70% EBA
10	100% EAA

11	10% EAA + 90% EBA
12	20% EAA + 80% EBA
13	30% EAA + 70% EBA
14	10% EAA + 90% EVA (9%VA)
15	20% EAA + 80% EVA (9%VA)
16	30% EAA + 70% EVA (9%VA)
17	10% EAA + 90% LLDPE
18	20% EAA + 80% LLDPE
19	30% EAA + 70% LLDPE
20	10% EMAA-1 + 90% PP
21	20% EMAA-1 + 80% PP
22	30% EMAA-1 + 70% PP
23	10% EAA + 90% PP
24	20% EAA + 80% PP
25	30% EAA + 70% PP
26 (COMPARISON)	100% EVA (9%VA)
27 (COMPARISON)	100% EBA
28 (COMPARISON)	100% LLDPE

Example 6 (performance evaluation of films of Example 5)

In order to evaluate the performance of a mono-layer film according to this invention comparative tests were run relating to the protein adhesion of the inventive films recited in Example 5 (which had EMAA) with respect to that of the comparative mono-layer films recited in Example 5 (which did not have any EMAA). This test differed from the protein adhesion test method described above in that instead of using turkey emulsion, chunks of turkey which had been cleaned up by removing the extraneous fat and other connective tissue such as partial removal of the sinews were used. (The chunks were cubes about 3 inches on a side, which is about 7.6 cm on a side.) The results are given in the following table:

Table VI
Protein Adhesion

<u>SAMPLE NUMBER</u>	<u>ADHESION INDEX*</u>	
	<u>MEAN</u>	<u>STANDARD DEVIATION</u>
1	No adhesion	
3	70.9	± 33.6
4	No adhesion	
6	32.6	± 12.3
7	No adhesion	
9	41.1	± 9.4
10	119.4	± 21.1
20	104.3	± 28.0

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26 (COMPARISON)	No adhesion
27 (COMPARISON)	No adhesion
28 (COMPARISON)	No adhesion

* Adhesion index = $\frac{\text{adhesion force of sample on Day n}}{\text{adhesion force of Comparison on Day n}} \times 100$

where the Comparison sample was ambient.

It is surprising that many of the above mono-layer films of the invention, as recited in Example 5, exhibited protein adhesion during cook-in, even though none was electron-beam irradiated.

While certain representative embodiments and details have been shown for the purpose of illustration, numerous modifications to the formulations described above can be made without departing from the invention disclosed.

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CLAIMS:

1. A flexible thermoplastic film suitable for protein-adhesion, cook-in packaging comprising a thermosealing layer of a copolymer of (i) an alpha-olefin having the formula $RCH=CH_2$ where R is H or C_1 to C_{20} alkyl, C_1 to C_{20} alkoxy, or C_6 aryl, and (ii) an alpha,beta-ethylenically unsaturated carboxylic acid.
5
2. The film of claim 1, wherein said copolymer of said thermosealing layer is selected from ethylene-methacrylic acid (EMMA) copolymers, ethylene-acrylic acid (EAA) copolymers, or mixtures thereof.
10
3. The film of claim 2, wherein said copolymer of said thermosealing layer is selected from ethylene-methacrylic acid (EMAA) copolymers with a methacrylic acid (MAA) content of about 4 to about 18% by weight, ethylene-acrylic acid (EAA) copolymers with an acrylic acid (AA) content of about 4 to about 22% by weight, or mixtures thereof.
15
4. The film of claim 2 wherein said EMAA copolymer is chosen from EMAA copolymers with an MAA content of about 9 to about 15% by weight, and said EAA copolymer is chosen from EAA copolymers with an AA content of about 6 to about 12% by weight.
20
5. The film of any one of claims 1 to 4 comprising at least one said thermosealing layer, a gas barrier layer and a structural layer.
25
6. The film of claim 5 wherein said gas barrier layer is selected from copolymers of vinylidene chloride with vinyl chloride or methyl acrylate or mixtures of the two, ethylene vinyl alcohol (EVOH) copolymers, polyamides or copolyamides or blends thereof with each other or with EVOH.
30

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any one of claims 1 to 9, removing air from inside the thus obtained package, sealing said package by sealing together at least two portions of said thermosealing layer facing each other and subjecting said sealed package to cooking at high
5 temperature, whereby said thermosealing layer adheres to said food product.

15. A cooked, protein-adhesion, cook-in package comprising a food product enveloped in said film of any one of claims 1 to 9, said film being sealed together by at least one
10 thermoseal at two portions of said thermosealing layer facing each other, said sealed package having been subjected to cooking at high temperature, whereby said thermosealing layer adheres to said food product.

16. Use of said film of any one of claims 1 to 9 for
15 making a protein adhesion cook-in package.

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